

BP Amoco (formerly Amoco Corporation, Resource Center)

Process to Lower the Cost of Olefin-Paraffin Separations

Light olefins, which are unsaturated, chemically active hydrocarbons, are the principal building blocks for the petrochemical industry. They are produced in greater quantities than any other organic chemicals and form the basis for many chemical products such as polyesters, surfactants, and antifreeze. Before they can be used in a product, light olefins such as ethylene and propylene must be purified by separating them from paraffins (a residue obtained from certain petroleum crudes). Traditionally, the U.S. olefins industry has used distillation processes to separate olefins from paraffins, but these processes are difficult and costly due to the extreme temperature and pressure conditions that are usually required.

In the 1970s, Amoco Corporation became interested in the facilitated transport process as an alternative to distillation processes. After conducting research, the company was able to demonstrate the technical feasibility of this process; however, it also experienced problems with its use. The complexing agent, silver nitrate, was costly, and cellulose acetate hollow-fiber bundles used for the contactor (the vessel used to bring the substances into contact) were not strong enough. Amoco suspended its research efforts, but by 1993, the price of silver had decreased and hollow-fiber technology had improved, making this an opportune time for the company to continue its research of the facilitated transport process. The project, which would also involve the testing of new chemical agents, was too risky for private investors, but the company believed it would be a good fit for the Advanced Technology Program (ATP). That year, Amoco applied for and was awarded cost-shared funding from ATP to develop a low-cost process for separating light olefins from the corresponding paraffins using facilitated transport and microporous polypropylene hollow-fiber contactors. Amoco believed this effort could result in increased earnings of more than \$60 million a year for the company from additional olefin recovery. Net benefits to U.S. chemical process industries were expected to approach approximately \$1 billion a year.

By the project's end in 1997, Amoco had successfully developed a high-efficiency contactor that could be used with silver nitrate. The company had also, with its subcontractor SRI International, developed two new complexing agents that were cost competitive with silver nitrate when used for facilitated transport. In spite of these successes, in 1998 Amoco discontinued its research into the new technology. The company had experienced costly operating problems with the new process and was unable to demonstrate its economic feasibility.

COMPOSITE PERFORMANCE SCORE

(based on a four star rating)

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Research and data for Status Report 93-01-0234 were collected during February 2003.

Early Tests of Facilitated Transport Identify Problems

Much of the cost of producing light olefins is associated with purifying the olefins by separating them from

paraffins (the residue from certain petroleum crudes). This step has traditionally been performed by distillation, which is usually achieved by refrigerating the olefins and paraffins at very low temperatures or by using trays to separate olefins from paraffins of the

same carbon number. Both methods are costly. Cryogenic refrigeration is capital and energy intensive, and the refrigeration compressors are expensive to maintain. Distillation with trays is capital intensive because it requires the use of many trays.

In the late 1970s, Amoco Corporation began to examine ways to improve its olefin-paraffin separation process in order to reduce costs. The company became interested in facilitated transport, a less costly alternative to distillation. With facilitated transport, a chemical agent, such as silver ion, is used to form a chemical association with electrons in the olefins. This association, formed inside a contactor, results in a water-soluble complex of olefins, which is transferred from the contactor to a second vessel where it is separated by lowering the pressure inside the vessel and/or by adding heat. Neither step requires an extreme of pressure or temperature.

To test this new technology, Amoco set up a facilitated transport pilot plant for olefin-paraffin separations. At the pilot plant, the company demonstrated the technical feasibility of the process; however, using silver nitrate as the complexing agent at high temperatures was costly. Moreover, cellulose acetate hollow-fiber bundles, which were used as the gas-liquid contactor in the process, weakened and burst with prolonged contact with the aqueous silver nitrate complexing agent. Because of these problems, Amoco suspended its development of the technology.

Market and Technological Changes Encourage Renewed Research

By 1994, the price of silver had decreased and advances had been made in hollow-fiber technology. Polypropylene fibers were available and contactors made from these fibers were rugged and could withstand high differential pressures, thereby improving the efficiency of olefin-paraffin separation. Based on these changes, Amoco believed it should resume its research and development effort to achieve a breakthrough in olefin-paraffin separation costs.

Amoco's goal was to develop a commercially viable process for separating and purifying light olefins, especially ethylene and propylene, using facilitated transport and microporous polypropylene hollow-fiber

contactors. The company also wanted to develop new water-soluble complexing agents.

Amoco recognized that developing this process would involve a high level of risk because the technology was new and would rely on the use of as-yet undeveloped chemical complexing agents. However, if successful, the company anticipated it would earn more than \$60 million per year from additional olefin recovery. Net benefits to the U.S. chemical process industries overall were expected to eventually approach \$1 billion per year. In addition, the cost savings resulting from this new technology would enable the U.S. olefins industry to gain a sustainable competitive advantage in the global marketplace.

Due to the risk involved in the project, as well as its potential for significant broad-based benefits, Amoco applied to ATP in 1993 for funding assistance and was awarded \$1.25 million for a three-year project.

New Separation Process Promises Broad-Based Benefits

Amoco believed that developing a facilitated transport process for olefin-paraffin separations would affect a wide range of technologies in the United States. The U.S. industries that would directly benefit from decreasing olefin costs included the polymer and petrochemical industries, as well as the packaging film, wire and cable coatings, toys, waste bags, chewing gum, squeeze bottles, electrical insulation, piping, blow-molded products, and injected-molded products industries.

Amoco's goal was to develop a commercially viable process for separating and purifying light olefins using facilitated transport

The lower cost and increased efficiency of olefin-paraffin separations would also increase the global competitiveness of the U.S. olefins industry. In 1994, the United States was the world's largest producer of ethylene, with an annual capacity of approximately 35 billion pounds. The global demand for this chemical was nearly 140 billion pounds per year and was predicted to grow by 4.4 percent through 1995. However, other areas of the world, including East Asia and the Middle

East, were steadily increasing their capacity to produce ethylene; this was expected to have a significant effect on the U.S. ethylene industry.

Emerging processes such as natural gas utilization, which was unprofitable at the time, would realize significant benefits from facilitated transport. Several of the technologies used to convert natural gas into liquid transportation fuel were capital intensive and yielded low rates of return. A facilitated transport process could greatly enhance the economics of these technologies to enable the production of olefins from domestic natural gas instead of imported oil. Thus, the success of Amoco's proposed research would not only help maintain the competitive position of U.S. industries, but could also lower U.S. dependence on imported oil.

Scientific and Technical Issues Are Identified

In order to make facilitated transport separations commercially viable, Amoco needed to address several critical scientific and technical issues. First, the complexing agent had to be stable, had to demonstrate chemical integrity, and could not degrade when heated. The complexing agent also had to be immune to poisoning by acetylenes and sulfur compounds, because process streams in the petrochemical industry were always contaminated with such compounds. Subcontractor SRI International had identified transition metal compounds that were thermally and chemically stable. The derivatives of these compounds could yield improved complexing agents, but developing an economical, large-scale synthesis of such compounds would be a technical challenge.

Cost savings resulting from this new technology would enable the U.S. olefins industry to gain a sustainable competitive advantage in the global marketplace.

Second, large, rugged contactor units containing porous polymer hollow fibers, which demonstrated high, sustainable olefin fluxes when processing impure olefin feedstreams, had to be developed. A porous polypropylene contactor manufactured by the Celgard Division of Hoechst Celanese was a promising candidate, but development work was needed to

demonstrate that it could be used in an industrial process stream for an extended period of time. One of Amoco's key concerns was the swelling of the fibers by aromatic hydrocarbons that were likely to be present in industrial process streams.

Third, integration of the facilitated transport process into existing olefins plants had to be tested. Successful pilot integration with an industrial facility was necessary for Amoco to realize the potential cost savings.

Improved Complexing Agents Tested at Bench-Scale Facility

To accomplish its goal, Amoco built an experimental bench-scale unit to test the separation of olefins from paraffins in various Amoco process streams using the facilitated transport process. At the same time, SRI conducted research to develop improved complexing agents. SRI was to synthesize and screen up to 10 new complexing agents and to deliver enough of the most promising complex for testing in Amoco's bench-scale unit.

In Amoco's experimental unit, two fiber bundles were used in an absorber/desorber arrangement. The operating temperature of each bundle was controlled through recirculating baths. A vacuum was used in the desorber to allow olefins to escape from the complexing agents while liquid pumps circulated the aqueous complexing agent solution.

In preliminary experiments, silver nitrate was used as a complexing agent because even though it was expensive, Amoco knew it would work. As other complexing agents became available through research at SRI, they were tested in the experimental unit. Initially, Amoco used synthetic mixtures of hydrocarbons to simulate the various process streams used in olefins plants and oil refineries. Poisoning studies were conducted by spiking the feeds with anticipated poisons (e.g., sulfides, acetylenes, or amines). These poisoning studies were considered essential in establishing the structural integrity of the complexing agents under the demanding conditions of an industrial environment. As progress was made, the company obtained actual feed samples from the plants and tested them in the experimental facility.

Facilitated Transport Requires Further Research

By the end of the project, Amoco had achieved two important objectives. First, silver nitrate could be used as a facilitating agent in the high-efficiency contactors manufactured by the Celgard Division of Hoechst Celanese. These contactors exhibited economic olefin fluxes and purity when processing impure olefin feedstreams in both bench-scale tests and initial pilot plant tests at an industrial site. Second, SRI had successfully developed two new complexing agents that were water soluble, were able to bind olefins under realistic operating conditions, and were cost competitive with silver nitrate when used for facilitated transport. Amoco tested each complex and deemed one candidate, molybdenum sulfide dimer, the best choice for further work because it had superior solubility, chemical stability, and shelf life.

Amoco was unable to demonstrate the economic feasibility of using this new technology.

However, work still remained on integrating the facilitated transport process into existing olefins plants. A pilot plant demonstration in a commercial olefins plant had to be completed; contactor and facilitating agent lifetimes had to be determined to accurately assess the economic viability of the technology; and a detailed productivity response to key process variables, such as temperature, pressures, transmembrane pressure, and flow rates, had to be precisely measured to determine optimal operating conditions.

Also, Amoco needed to demonstrate that the alternative complexing agent candidate was effective on both the smaller bench scale and the pilot plant scale. Finally, additional research on poison resistance and more effective complexing agents was needed. This area demonstrated great promise, but the technical risks were still quite high.

Amoco Discontinues Separation Process Development

For a year after the ATP funding ended, Amoco continued its research of facilitated transport for olefin-paraffin separations using both the silver nitrate

complexing agent and molybdenum sulfide dimer. In work on the technology. Although the process was technically sound, the company was experiencing costly operating problems. The hollow-fiber contactors were not robust enough, and the candidate complexing agent was expensive. Furthermore, the hollow fibers and limited thermal stability failed to alleviate the problems with silver nitrate that the company had experienced prior to the project, such as susceptibility to sulfide and acetylene poisoning. Thus, Amoco was unable to demonstrate the economic feasibility of using this new technology for olefin-paraffin separations.

Knowledge Disseminated Through Presentation and Patents

Based on its work on the ATP-funded project, Amoco made a presentation entitled "Facilitated Transport Process for Low-Cost Olefin-Paraffin Separations" at the ATP Catalysis, Biocatalysis, & Separations Technology Review in October 1996. Amoco has also been granted three patents as a result of its work on the project.

Conclusion

By the end of the ATP-funded project, Amoco had achieved several of its objectives. It was able to use silver nitrate as a facilitating agent in high-efficiency contactors and had developed a promising new complexing agent that would potentially cost less than silver nitrate when used for facilitated transport. However, the company was unable to demonstrate the commercial viability of separating olefins from paraffins using facilitated transport. Thus, it did not commercialize the technology. Nevertheless, Amoco believes that the knowledge it gained from the ATP-funded project, especially about chemical agents, may be useful in future studies on separation.

PROJECT HIGHLIGHTS

BP Amoco (formerly Amoco Corporation, Resource Center)

Project Title: Process to Lower the Cost of Olefin-Paraffin Separations (Facilitated Transport Process for Low-Cost Olefin-Paraffin Separations)

Project: To capitalize on recent advances in chemistry and hollow-fiber manufacture to develop a new, low-cost process for separating light olefins from the corresponding paraffins.

Duration: 4/15/1994-4/14/1997

ATP Number: 93-01-0234

Funding** (in thousands):

ATP Final Cost	\$1,250	50%
Participant Final Cost	<u>1,250</u>	50%
Total	\$2,500	

Accomplishments: By the end of the project, Amoco had achieved the following objectives:

- Developed a high-efficiency contactor that could be used with silver nitrate and established olefin flux targets under realistic operating conditions. The target flux, recovery, and separation factors were achieved and surpassed at the laboratory bench scale.
- Developed two new promising complexing agents through a subcontract with SRI International. After testing each complexing agent, Amoco decided to continue development of one of them, molybdenum sulfide dimer, because of its superior solubility, chemical stability, and shelf life.

In addition, Amoco made a presentation entitled "Facilitated Transport Process for Low-Cost Olefin-Paraffin Separations" at the ATP Catalysis, Biocatalysis, & Separations Technology Review in Boulder, Colorado in October 1996.

Since 1998, Amoco has been granted the following patents:

- "Unsaturated hydrocarbon separation and recovery process"
(No. 5,744,685: filed October 15, 1996, granted April 28, 1998)

- "Unsaturated hydrocarbon separation and recovery process"
(No. 5,863,420: filed October 15, 1996, granted January 26, 1999)
- "Process for synthesis of molybdenum sulfide dimers"
(No. 5,962,364: filed July 30, 1997, granted October 5, 1999)

Commercialization Status: The chemical agents that were developed during this ATP-funded project have not been commercialized.

Outlook: At this time, it is unclear whether the chemical agents developed during this ATP-funded project can be economically applied to olefin-paraffin separations with facilitated transport. However, Amoco believes that the knowledge gained about the chemical agents may be useful in future studies on separation.

Composite Performance Score: * *

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** As of December 9, 1997, large single applicant firms are required to pay 60% of all ATP project costs. Prior to this date, single applicant firms, regardless of size, were required to pay indirect costs.